

TOPIC 15 – ENERGETICS

15.4: SPONTANEITY

IB Chemistry
T15D13



15.4 Spontaneity - 2.5 hours

- 15.4.1 Predict whether a reaction or process will be spontaneous by using the sign of ΔG . (3)
- 15.4.2 Calculate ΔG for a reaction using the equation $\Delta G = \Delta H - T\Delta S$ and by using values of the standard free energy change of formation, ΔG_f° . (2)
- 15.4.3 Predict the effect of a change in temperature on the spontaneity of a reaction using standard entropy and enthalpy changes and the equation $\Delta G = \Delta H - T\Delta S$. (3)



15.4.1 - Spontaneity

- 15.4.1 Predict whether a reaction or process will be spontaneous by using the sign of ΔG . (3)
- Chemists often inquire to whether a chemical reaction (or even physical change) is spontaneous under standard conditions.
- A **spontaneous** process is one which has a natural tendency to occur. A spontaneous process involves an increase in the entropy of the universe



15.4.1 – Initiation of Reactions

- Spontaneous processes may need no initiation:
 - The evaporation of water
 - The dissolving of sucrose in water to form a solution
 - The diffusion of gases
- Some may need initiation:
 - Hydrogen reacts rapidly with oxygen to form water if small brief spark is applied
 - Carbon reacts with the oxygen in the air when ignited. The reaction then produces its own heat



Some spontaneous processes occur very quickly,
others very slowly

15.4.1 – Non-spontaneous Reactions

- Some reactions are NON-spontaneous, for example:
 - Copper does not react with dilute hydrochloric acid and water does not freeze (at STdP)
 - A non-spontaneous reaction would result in a decrease in the entropy of the universe
- Non-spontaneous processes can become spontaneous when the temperature is increased or when energy is supplied continuously from an external source
 - Decomposition of H_2O into H_2 and O_2 becomes spontaneous when electrical current is applied



15.4.1 – Gibbs Free Energy

- The **spontaneity** of a process or chemical reaction is determined by the sign of the **Gibbs free energy change**, ΔG^θ . It is calculated from the following relationship:
 - $\Delta G^\theta = \Delta H^\theta - T\Delta S^\theta$
 - T represents the absolute temperature
 - ΔS^θ represents the entropy change occurring in the system
 - ΔH^θ represents the enthalpy change



15.4.1 – Gibbs Free Energy Values

- The Gibbs free energy change as a criterion for spontaneity is summarized as follows:
 - If ΔG^θ is **negative**, then the reaction or process will be spontaneous
 - If ΔG^θ is **positive**, then the reaction or process will be non-spontaneous
 - If ΔG^θ is **zero**, then the reaction or process will be at equilibrium (the rate of forward reaction will be the rate of backward reaction.)



15.4.1 – Gibbs Free Example

- Calculate the Gibbs free energy change for the following reaction under standard state conditions



$$\Delta H^\theta = -95.4 \text{ —}$$

$$\Delta S^\theta = -198.3 \text{ —}$$

$$T = 298\text{K}$$

$$\Delta G^\theta = \Delta H^\theta - T\Delta S^\theta$$

$$\Delta G^\theta = (-95.4 \text{ —}) - [(298\text{K}) (-198.3 \text{ —})]$$

$$\Delta G^\theta = -36.6 \text{ — (spontaneous)}$$



15.4.1 – Gibbs Calculation

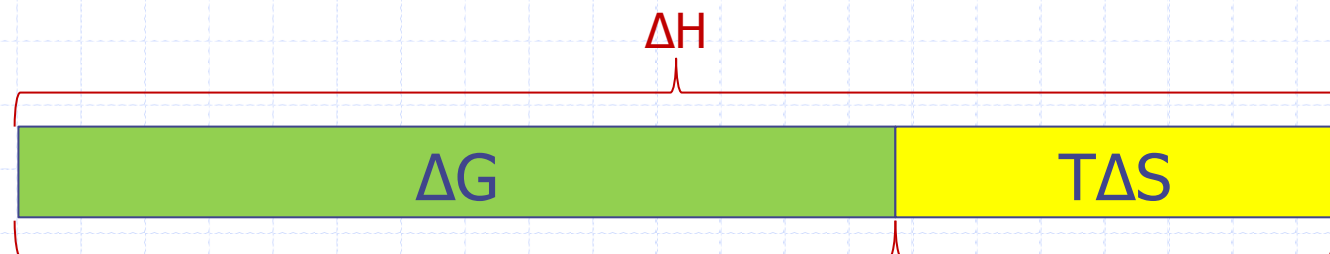
- In the previous problem the reaction was spontaneous as $\Delta G^\theta = -36.6$ —
- If you wanted to calculate the temperature above which the reaction ceases to occur spontaneously
 - $\Delta G^\theta = 0 = \Delta H^\theta - T\Delta S^\theta$
 - $\Delta H^\theta = T\Delta S^\theta$
 - $T = \frac{\Delta H^\theta}{\Delta S^\theta} = 481 \text{ K} = 208^\circ\text{C}$



15.4.1 – What is “free” energy?

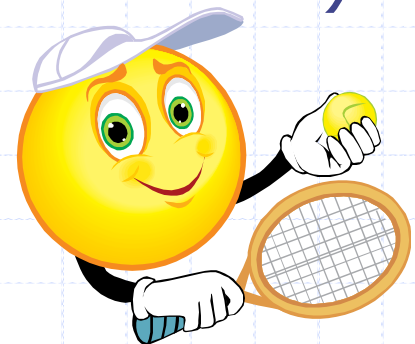
- What is ‘free energy?’ $\Delta G^\theta = \Delta H^\theta - T\Delta S^\theta$
- The Gibbs free energy refers to the maximum amount of non-expansion work that can be done by a system.
 - Non-expansion work is termed “useful” work
 - $T\Delta S$ (which has units of energy) is not able to do work and can be regarded as ‘un-free energy,’ as it’s dispersed into the random motion of particles

total energy change at constant temperature



15.4.1 – 'Free' energy analogy

- A useful analogy that Talbot gives refers to a game of squash or tennis.
 - The heat energy lost through perspiration (sweat) is not useful energy, rather it is the energy to hit the ball which is 'free' to do useful work.
 - Work is done when a force moves an object through a distance (in the direction of the force)



15.4.1 – Example #2

- Calculate the entropy change of the surroundings when water condenses on a window at 25°C T
 - $\text{H}_2\text{O (g)} \rightarrow \text{H}_2\text{O (l)}$
 - $\Delta H^\theta = -44.0 \text{ —}$
 - $\Delta S^\theta_{\text{system}} = -118 \text{ —}$
 - $\Delta S_{\text{surroundings}} = - \text{ — } = \text{ — } = +147.7 \text{ —}$
 - Entropy change for surroundings is positive (favorable), but the entropy change in the system is negative (unfavorable).
 - Overall entropy: $\Delta S^\theta_{\text{universe}} = \Delta S^\theta_{\text{system}} + \Delta S^\theta_{\text{surroundings}}$
 - $\Delta S^\theta_{\text{universe}} = -118 \text{ — } + 147.7 \text{ — } = 29.7 \text{ —}$



15.4.1 – Example #2 Cont...

- Spontaneity can also be predicted by calculating the Gibbs free energy change, ΔG^θ :
 - $\Delta G^\theta = \Delta H^\theta - T\Delta S^\theta$
 - $\Delta G^\theta = (-44 \text{ —}) - [(298\text{K}) \times (-118 \text{ —})]$
 - $\Delta G^\theta = -79.2 \text{ —}$
 - A negative value for ΔG^θ , and a positive value for $\Delta S^\theta_{\text{universe}}$ are equivalent criteria for spontaneity



15.4.2 – Gibbs Free Energy

Change of Formation ΔG^{θ}_f

- 15.4.2 Calculate ΔG for a reaction using the equation $\Delta G = \Delta H - T\Delta S$ and by using values of the standard free energy change of formation, ΔG_f . (2)
- Each compound has a Gibbs free energy of formation, ΔG^{θ}_f .
- This is the free energy change that occurs when one mole of a compound is formed from its elements in their standard states under standard conditions



15.4.2 - ΔG^θ_f for compounds

- For example, the Gibbs free energy change of formation of water and benzene:
 - $\text{H}_2 (\text{g}) + \frac{1}{2} \text{O}_2 (\text{g}) \rightarrow \text{H}_2\text{O} (\text{l}) \quad \Delta G^\theta_f = -51 \text{ —}$
 - $6\text{C} (\text{s}) + 3\text{H}_2 (\text{g}) \rightarrow \text{C}_6\text{H}_6 (\text{l}) \quad \Delta G^\theta_f = +49 \text{ —}$
 - Some values are listed on pages 12&13 of the IB Data Booklet

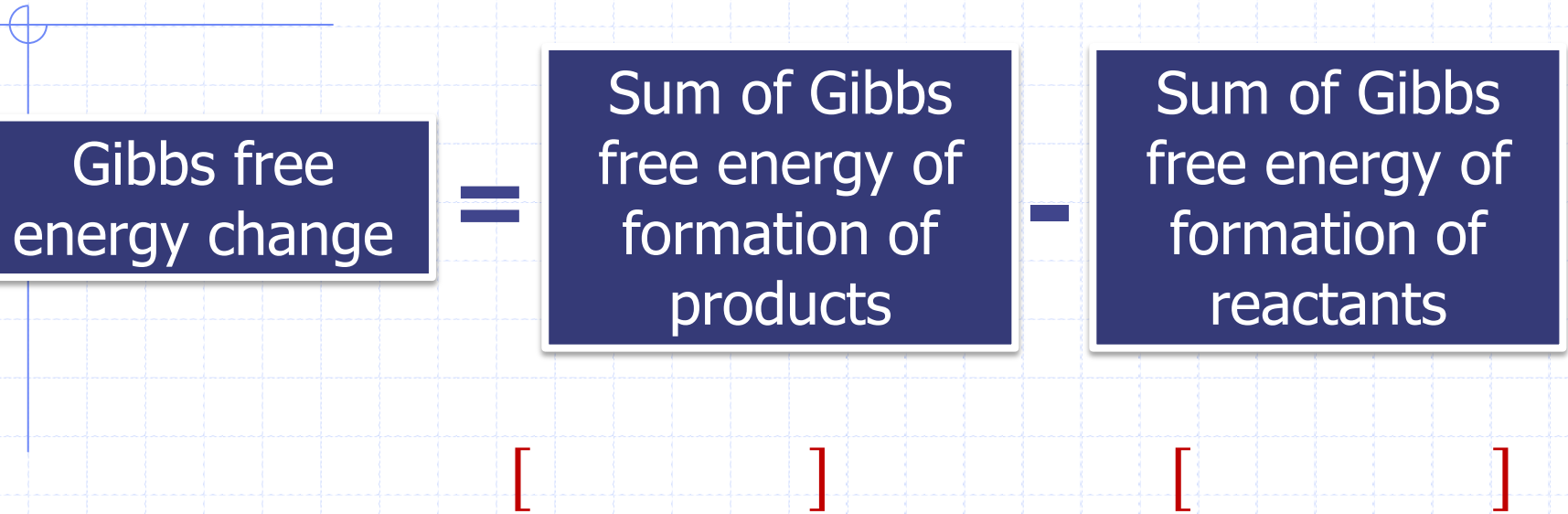


15.4.2 – Values of ΔG^θ_f

- ΔG^θ_f is a measure of a compound's stability compared to its elements
- Compounds that have a $\Delta G^\theta_f < 0$ are more thermodynamically stable than their elements
 - The compound can therefore be synthesized from its elements and there is no tendency for it to decompose back into the elements
- Compounds that have a $\Delta G^\theta_f > 0$ are less thermodynamically stable than their elements
 - The compound cannot be synthesized from its elements and has a tendency for it to decompose back into its constituent elements.



15.4.2 – Gibbs free for Reaction



The diagram illustrates the equation for Gibbs free energy change. It features three dark blue rectangular boxes with white text, connected by mathematical symbols. The first box on the left is labeled 'Gibbs free energy change'. To its right is an equals sign (=). The second box is labeled 'Sum of Gibbs free energy of formation of products'. To its right is a minus sign (-). The third box is labeled 'Sum of Gibbs free energy of formation of reactants'. Below each of these three boxes is a pair of red square brackets []. A blue line with a small circle at its top end is positioned to the left of the first box, extending vertically.

$$\text{Gibbs free energy change} = \text{Sum of Gibbs free energy of formation of products} - \text{Sum of Gibbs free energy of formation of reactants}$$

[] []



15.4.2 – Example #3

- Use the following Gibbs free energy change of formation, ΔG^θ_f , for the decomposition of magnesium carbonate



- $\Delta G^\theta_f[\text{MgCO}_3(\text{s})] = -1012 \text{ —}$

- $\Delta G^\theta_f[\text{MgO}(\text{s})] = -569 \text{ —}$

- $\Delta G^\theta_f[\text{CO}_2(\text{g})] = -394 \text{ —}$

- $\Delta G^\theta_f = [(-569 + (-394))] - (-1012) = +49 \text{ —}$



The + sign of ΔG indicates that the reaction is non-spontaneous under standard conditions

15.4.3 – Spontaneity and Temperature

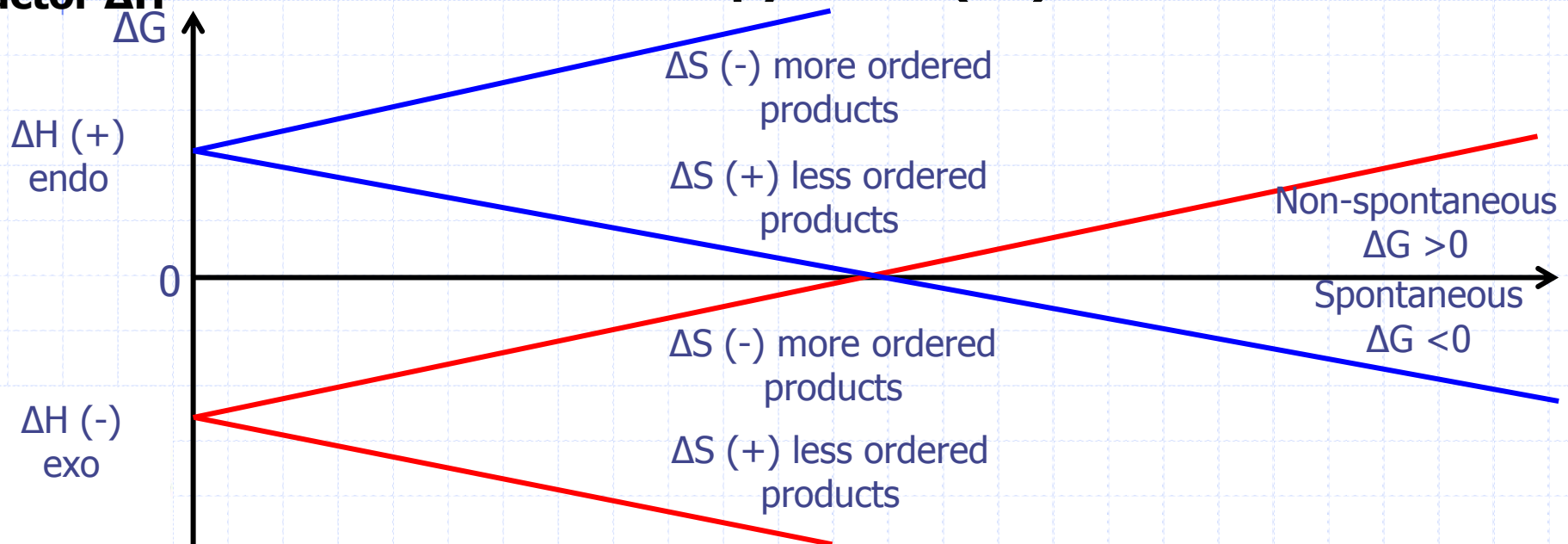
- 15.4.3 Predict the effect of a change in temperature on the spontaneity of a reaction using standard entropy and enthalpy changes and the equation $\Delta G = \Delta H - T\Delta S$. (3)
- The Gibbs equation results in four different types of reaction depending on ΔH and ΔS of the system.
- Positive entropy values help drive a reaction
- Negative enthalpy values help drive a reaction



Enthalpy change ΔH	Entropy Change ΔS	Gibbs Free energy change ΔG	Spontaneity
Positive (endo)	Positive (products more disordered)	Depends on T	Spontaneous at high T, $T\Delta S > \Delta H$
Positive (endo)	Negative (products less disordered)	Always Positive	Never spontaneous
Negative (exo)	Positive (products more disordered)	Always Negative	Always spontaneous
Negative (exo)	Negative (products less disordered)	Depends on T	Spontaneous at low T, $T\Delta S < \Delta H$

Enthalpy
Factor ΔH

Effect of entropy factor (ΔS) as T increases



15.4.3 – Effect of T on Spontaneity

- Using example values for ΔH^θ and ΔS^θ we can calculate the Gibbs free energy change for reactions at different temperatures (10K-10000K) for positive and negative values of each.
 - ΔH^θ and ΔS^θ both positive
 - ΔH^θ positive and ΔS^θ negative
 - ΔH^θ negative and ΔS^θ positive
 - ΔH^θ and ΔS^θ both negative



15.4.3 - ΔH^θ and ΔS^θ both positive

- $\Delta H^\theta = 200 \text{ —}$ and $\Delta S^\theta = 200 \text{ —}$
- At $T = 10\text{K}$
 - $\Delta G^\theta = 200 \text{ —} - (10\text{K} \times 0.2 \text{ —}) = +198 \text{ —}$
- At $T = 10000\text{K}$
 - $\Delta G^\theta = 200 \text{ —} - (10000\text{K} \times 0.2 \text{ —}) = -1800 \text{ —}$
- This corresponds to the first row in the previous table. The sign of ΔG^θ depends on the Temperature and is spontaneous at high temperatures, when $T\Delta S > \Delta H$



15.4.3 - ΔH^θ positive and ΔS^θ negative

- $\Delta H^\theta = 200$ — and $\Delta S^\theta = -200$ —
- At $T = 10\text{K}$
 - $\Delta G^\theta = 200$ — - $(10\text{K} \times -0.2\text{ —}) = +202$ —
- At $T = 10000\text{K}$
 - $\Delta G^\theta = 200$ — - $(10000\text{K} \times -0.2\text{ —}) = +2200$ —
- This corresponds to the second row in the previous table. The sign of ΔG^θ is always positive and reaction is never spontaneous



15.4.3 - ΔH^θ negative and ΔS^θ positive

- $\Delta H^\theta = -200$ — and $\Delta S^\theta = 200$ —
- At $T = 10\text{K}$
 - $\Delta G^\theta = -200$ — - $(10\text{K} \times 0.2$ —) = -202 —
- At $T = 10000\text{K}$
 - $\Delta G^\theta = -200$ — - $(10000\text{K} \times 0.2$ —) = -2200 —
- This corresponds to the third row in the previous table. The sign of ΔG^θ is always negative and reaction is always spontaneous



15.4.3 - ΔH^θ and ΔS^θ both negative

- $\Delta H^\theta = -200 \text{ —}$ and $\Delta S^\theta = -200 \text{ —}$
- At $T = 10\text{K}$
 - $\Delta G^\theta = -200 \text{ —} - (10\text{K} \times -0.2 \text{ —}) = -198 \text{ —}$
- At $T = 10000\text{K}$
 - $\Delta G^\theta = -200 \text{ —} - (10000\text{K} \times -0.2 \text{ —}) = +1800 \text{ —}$
- This corresponds to the last row in the previous table. The sign of ΔG^θ depends on the temperature and the reaction is spontaneous at low temperatures when, $T\Delta S < \Delta H$

